Transformation of Iron Oxide and Hydroxide Phases and its Effects on Contaminant Mobility

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Introduction

Iron oxides and hydroxides [iron (hydro)oxides] are one of the most common phases in the earth’s crust. Due to their ubiquity in the natural environment, they have long been recognized for their ability to regulate the concentrations of hazardous elements in nature. Furthermore, the relative ease with which they can be synthesized under controlled conditions has made them attractive materials for industrial applications like water-treatment and contaminant remediation.

Iron (hydro)oxides, in particular, are expected to play an important role in controlling the release of radionuclides from geological disposal environments. One of radionuclides present in spent fuel wastes is Se-79, which exists as highly mobile Se(IV) oxyanions under alkaline and partly reducing conditions expected in geological repositories. The iron (hydro)oxides present in steel corrosion products as well as in the surrounding host rock could provide a pathway to immobilize it. However, the long-term behavior of radionuclides like Se-79 is strongly dependent on the transformation of iron (hydro)oxide substrates, which, in turn is also affected by the presence of other foreign ligands in the system. One of the most important ligands known to affect iron (hydro)oxide transformation is Si, which is derived from the dissolution of the vitrified waste form as well as from the surrounding silicate host rock. Taking into account the influence of iron (hydro)oxide transformation as well as that of foreign ligands is important to formulate more reliable safety cases to predict the long-term stability of waste disposal environments.

Objectives

The objectives of this study are to (1) understand the effects of Si on the transformation kinetics of iron (hydro)oxides, (2) to understand the behavior of Se(IV) during the transformation of iron (hydro)oxides and (3) determine the effects of Si on the behavior of Se during iron (hydro)oxide transformation.

Methods

The primary method used in this study is the aqueous synthesis of iron (hydro)oxides. This was accomplished by base hydrolyzing solutions containing aqueous Fe(III) ions. In the experiments, investigating the effect of Si on ferrihydrite transformation, Si was included in the solutions along with Fe(III). In the experiments investigating the behavior of Se, during ferrihydrite transformation, Se(IV) was included in the aqueous solutions

Solid products were characterized using a variety of spectroscopic techniques, such as x-ray diffraction, infrared and x-ray absorption spectroscopy. Concentrations of elements in solutions were determined spectroscopically using inductively-coupled plasma atomic emission spectroscopy.

Results and Discussion

Effect of Si on iron (oxy)hydroxide transformation

The presence of Si in the system significantly modified the transformation from ferrihydrite to goethite and hematite. Fig. 1 shows the apparent activation energies of crystallization for goethite and hematite. The increase in the apparent activation energies indicates the retardation of crystallization for both phases. This retardation effect is due to Si sorption inhibiting the dissolution of ferrihydrite (prerequisite for goethite crystallization) and the introduction of negative electrostatic charge on ferrihydrite surfaces, which inhibits particle aggregation (prerequisite to hematite crystallization).

Behavior of Se(IV) during iron (oxy)hydroxide transformation

Co-precipitation of Se(IV) with ferrihydrite resulted in a significant removal of Se(IV) from solution both in acidic and alkaline conditions. As can be seen in Fig. 2, >90%
Retention of Se(IV) in the freshly co-precipitated and post-transformation solids of Se(IV) was taken up by ferrihydrite immediately after co-precipitation. However, following transformation, the amount of Se(IV) in the solid decreased markedly at alkaline conditions, indicating the release of Se(IV) back into solution. This difference in the retention behavior of Se(IV) at different pH may be explained by the differences in transformation pathway of ferrihydrite. At pH 5, the ferrihydrite is not very susceptible to dissolution, which results in the dominance of hematite in its post-transformation phase assemblage. In contrast, the solubility of ferrihydrite is much higher, resulting in the formation of goethite. The increased dissolution of ferrihydrite at pH 10 likely resulted in the release of Se(IV) into solution.

Results of XAS analysis of the post-transformation solids are consistent with the Se(IV) being present primarily as an inner-sphere adsorption complex (Table 1). Given that Se(IV) adsorbs poorly on iron (oxy)hydroxide surfaces at alkaline conditions, the retention mechanism of Se(IV) may also explain the decreased retention at pH 10.

Table 1. Results of XAS analysis. CN stands for coordination number.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Path</th>
<th>CN</th>
<th>R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 5</td>
<td>Se-O</td>
<td>2.6±0.1</td>
<td>1.70±0.01</td>
</tr>
<tr>
<td>Fresh</td>
<td>Se-Fe</td>
<td>1.4±0.4</td>
<td>3.25±0.05</td>
</tr>
<tr>
<td>pH 5</td>
<td>Se-O</td>
<td>2.3±0.1</td>
<td>1.72±0.01</td>
</tr>
<tr>
<td>Trans</td>
<td>Se-Fe</td>
<td>2.1±0.4</td>
<td>3.29±0.05</td>
</tr>
<tr>
<td>pH 10</td>
<td>Se-O</td>
<td>2.8±0.1</td>
<td>1.68±0.01</td>
</tr>
<tr>
<td>Fresh</td>
<td>Se-Fe</td>
<td>0.9±0.4</td>
<td>3.32±0.05</td>
</tr>
<tr>
<td>pH 10</td>
<td>Se-O</td>
<td>2.8±0.1</td>
<td>1.68±0.01</td>
</tr>
<tr>
<td>Trans</td>
<td>Se-Fe</td>
<td>2.6±0.4</td>
<td>3.37±0.05</td>
</tr>
</tbody>
</table>

Effect of Si on the behavior of Se(IV) during iron (oxy)hydroxide transformation

Drawing from the insights presented in the previous sections, this part of this thesis focuses on the effect of Si on the behavior of selenite during ferrihydrite transformation. Results show that the effect of Si is two-fold. As seen in Fig. 3, the presence of Si slows down the release of Se(IV) back into solution. However, the presence of Si also results in the release of more Se(IV) back into solution. The first effect may be explained by the inhibition of ferrihydrite dissolution, which also inhibits the release of Se(IV) in solution. The second effect may be understood in terms of competition between Si and Se(IV) for adsorption sites on goethite and hematite surfaces.

Conclusions

As seen in this investigation, the transformation of iron (oxy)hydroxides is heavily influenced by the presence of another ligand in the system (i.e. Si). Additionally, the transformation behavior of iron (oxy)hydroxides also impacts the behavior of oxyanion species such as Se(IV). In turn, the presence of Si in the system impacts the overall and long-term behavior of Se(IV). These findings have significant implications on the behavior of radionuclides that maybe released from waste disposal systems and as such, must be considered in safety assessment.